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[TITLE OF DOCUMENT] SCOPE OF CLAIMS

[CLAIM 1]

An embossed release paper for synthetic leather production, comprising at least paper as a support and an ionizing radiation cured film provided on the paper, the upper part of the cured film having been embossed, characterized in that the cured film has been formed by applying an ionizing radiation to a coating material comprising at least an ionizing radiation curing composition having a softening point of 40°C or above, to cure the ionizing radiation curing composition, the ionizing radiation curing composition comprising a product of a reaction of an isocyanate compound with an (meth)acrylic compound containing an (meth)acryloyl group and reactive with the isocyanate compound.

[CLAIM 2]

An embossed release paper for synthetic leather production, comprising at least paper as a support and an ionizing radiation cured film provided on the paper, the upper part of the cured film having been embossed, characterized in that the cured film has been formed by applying an ionizing radiation to a coating material comprising at least an ionizing radiation curing composition having a softening point of 40°C or above, to cure the ionizing radiation curing composition, the ionizing radiation curing composition comprising a product of a reaction of an isocyanate compound with an (meth)acrylic compound containing an (meth)acryloyl group and reactive with the isocyanate compound, and a compound free from an (meth)acryloyl group and reactive with an isocyanate group.

[CLAIM 3]

The embossed release paper according to claim 1 or 2, wherein the coating material further comprises 1 to 70% by weight of a film forming resin.

[CLAIM 4]

The embossed release paper according to claim 1 or 2, wherein the coating material further comprises 0.5 to 20% by weight of a silicone compound.

[CLAIM 5]

The embossed release paper according to any one of claims 1 to 4, wherein a seal layer comprising an inorganic pigment and a film forming resin is provided on the surface of the support.

[CLAIM 6]

The embossed release paper according to any one of claims 1 to 5, wherein the ionizing radiation cured film has a multilayer structure of at least two layers.

5 [CLAIM 7]

The embossed release paper according to claim 6, wherein, in the ionizing radiation cured film having a multilayer structure of at least two layers, 0.5 to 50% by weight of an inorganic pigment is contained in one or at least two layers.

10 [CLAIM 8]

The embossed release paper according to claim 6 or 7, wherein, in the ionizing radiation cured film having a multilayer structure of at least two layers, 0.5 to 50% by weight of an inorganic pigment is contained in the lowermost layer.

15 [CLAIM 9]

The embossed release paper according to any one of claims 6 to 8, wherein, in the ionizing radiation cured film having a multilayer structure of at least two layers, 0.5 to 20% by weight of a silicone compound is contained in one or at least two layers.

20 [CLAIM 10]

The embossed release paper according to any one of claims 6 to 9, wherein, in the ionizing radiation cured film having a multilayer structure of at least two layers, 0.5 to 20% by weight of a silicone compound is contained in the uppermost layer.

25 [CLAIM 11]

The embossed release paper according to any one of claims 6 to 10, wherein, in the ionizing radiation cured film having a multilayer structure of two or more layers, 0.5 to 50% by weight of an inorganic pigment is contained in the lowermost layer, and 0.5 to 20% by weight of a silicone compound is contained in the uppermost layer.

30 [CLAIM 12]

The embossed release paper according to any one of claims 6 to 11, wherein, in the ionizing radiation cured film having a multilayer structure of two or more layers, 0.5 to 50% by weight of an inorganic pigment is contained in the lowermost layer, and 0.5 to 20% by weight of a silicone compound is contained in each layer.

35 [CLAIM 13]

The embossed release paper according to any one of claims 1 to 11, wherein the paper as the support is neutral paper.

[CLAIM 14]

The embossed release paper according to any one of claims 5 1 to 13, wherein the paper as the support has been embossed.

[CLAIM 15]

A process for producing an embossed release paper according to any one of claims 1 to 14, characterized by comprising the steps of: coating a coating liquid, diluted with 10 to 1000 parts by weight of the solvent based on 100 parts by weight on a solid basis of the coating material having a softening point of 40°C or above, onto a surface of a support at a coverage of 1 to 40 g/m² on a dry basis to form a coating film; vaporizing the solvent from the coating film to dry the coating film; and applying an ionizing radiation to the coating film to form an ionizing radiation cured film after embossing either the dried coating film or the support and the dried coating film simultaneously.

[TITLE OF DOCUMENT] SPECIFICATION

[TITLE OF INVENTION] EMBOSSED RELEASE PAPER AND PROCESS
20 FOR PRODUCING THEREOF

[Technical Field]

[0001] The present invention relates to an embossed release paper and a process for producing thereof. More particularly, the present invention relates to an embossed release paper using an ionizing radiation curing coating material having a specific composition. The embossed release paper is useful for producing the synthetic leather as a release paper which has excellent embossability, heat resistance and separability.

[Background Art]

[0002] An embossed release paper has hitherto been used as an in-process release paper for a synthetic leather. Further, for example, polyurethane (PU), polyvinyl chloride (PVC), and a combination of PU with PVC are known as materials for synthetic leathers. A PU leather has been produced, for example, by coating a PU resin paste for a skin layer onto a release paper, drying and solidifying the coating at a temperature of 110 140°C, applying the assembly to a backing fabric with the aid of a two-component curing type PU-based adhesive,

allowing a reaction to proceed in a curing room of 5 to 70°C for 2 to 3 days, and peeling off the release paper. In this process, in general, PU resins dissolvable in organic solvents have been used. In recent years, however, aqueous PU resins have become used in consideration of environmental problems. In this case, drying is sometimes carried out at a high temperature of 150 to 180°C. A PVC leather has been produced, for example, by coating a PVC sol onto a release paper, heating the coating at 200 to 250°C to cause gelation, then forming a PVC expanded layer, applying the assembly to a backing fabric, and then peeling off the release paper. A leather comprising a combination of PU with PVC (a semisynthetic leather) has been produced, for example, by coating a PU resin paste for a skin layer onto a release paper, drying and solidifying the coating, then applying the assembly to a backing fabric, and then peeling off the release paper. Further, a split leather comprising any of these synthetic leathers to a natural leather is also known.

[0003] In the production of PVC leathers and semisynthetic leathers, a release paper produced by coating a silicone resin and embossing the coating to impart a concave-convex pattern is generally used. The release paper is used at the temperature of 220 °C during processing. However the use of this release paper is disadvantageous in that the embossability is poor and uneven gloss is likely to occur, making it difficult to repeatedly use the release paper.

[0004] In the production of PU leathers, since the film forming temperature of PU is below that of PVC, a release paper produced by extrusion coating a thermoplastic resin such as polypropylene or 4-methyl-1-pentene and then embossing the coating is used. The release paper for PU leathers has an excellent embossing capability for PU, is also good in releasability in the production of synthetic leathers using a two-component curing-type PU, and can be repeatedly used a number of times, but on the other hand, this release paper is disadvantageous in that, since the material for the release paper is a thermoplastic resin, the heat resistance is so low. Due to the above problem, the release paper produced by extrusion coating of a thermoplastic resin has been used only in a part of the PVC leather and semisynthetic leather production, and, up to now, any release paper usable in both PVC leathers and PU leathers has not been developed.

[0005] In recent years, a release paper, on which an embossed mark is casted, using an electron beam curing resin such as isodecyl acrylate, which is excellent in not only embossing capability but also heat resistance, has become used in both PU and PVC (Patent Document No.

5 1). The above release paper, however, is disadvantageous in that an isocyanate in a curing agent used in a two-component curing-type PU is reacted with an electron beam curing resin on the surface of release paper, and, consequently, the separation of the release paper is difficult. Further, the strength of paper is deteriorated upon electron beam 10 irradiation, and thus the release paper has lowered heat resistance and durability. Furthermore, since the coverage of the electron beam curing resin is large and 40 to 150 g/m², the production cost of the release paper is very high.

15 [0006] A release paper using a resin composed mainly of a compound containing an ethylenically unsaturated bond such as an epoxy acrylate resin curable upon exposure to an ionizing radiation has also been proposed. As in the release layer described above, up to now, this embossed release paper has not been put to practical use yet due to the difficulty of separating the two-component curing-type PU 20 material (Patent Document No. 2).

25 [0007] Further, in order to improve the heat resistance of the release paper and the releasability involved in the use of two-component curing-type PU, a method has been proposed in which an acryloyl group-containing silicone resin is used. In the above release paper, the resin as the starting material is expensive, and, further, the separability and processability are poor. Consequently, up to now, the release paper has not been put to practical use (Patent Documents Nos.3 and 4).

[0008]

30 [Patent Document No. 1] Japanese Patent Laid-Open No. 2780/1988

[Patent Document No. 2] Japanese Patent Laid-Open No. 10626/1989

35 [Patent Document No. 3] Japanese Patent Laid-Open No. 269931/1993

[Patent Document No. 4] Japanese Patent Laid-Open No. 62958/2001

[DISCLOSURE OF THE INVENTION]

[Problem to Be Solved by the Invention]

5 [0009] As mentioned thus above, it becomes imperative to develop an embossed release paper which has excellent heat resistance and separability from a two-pack curing type adhesive, that is, can be applied in the production of all of synthetic leathers, excellent releasability after repeated use and embossability, and can be obtained at low cost. The present inventors have intensively studied and, as a result, have solved the above problem.

10 [Means for Solving the Problem]

[0010] According to the present invention, there is provided an embossed release paper for synthetic leather production, comprising at least paper as a support and an ionizing radiation cured film provided on the paper, the upper part of the cured film having been embossed, characterized in that the ionizing radiation cured film has been formed by applying an ionizing radiation to a coating material comprising at least an ionizing radiation curing composition having a softening point of 40°C or above, to cure the ionizing radiation curing composition, the ionizing radiation curing composition comprising a product of a reaction of an isocyanate compound with an (meth)acrylic compound containing an (meth)acryloyl group and reactive with the isocyanate compound.

[0011] Further, according to another aspect of the present invention, there is provided an embossed release paper for synthetic leather production, comprising at least paper as a support and an ionizing radiation cured film provided on the paper, the upper part of the cured film having been embossed, characterized in that the ionizing radiation cured film has been formed by applying an ionizing radiation to a coating material comprising at least an ionizing radiation curing composition having a softening point of 40°C or above, to cure the ionizing radiation curing composition, the ionizing radiation curing composition comprising a product of a reaction of an isocyanate compound with an (meth)acrylic compound containing an (meth)acryloyl group and reactive with the isocyanate compound, and a compound free from an (meth)acryloyl group and reactive with an isocyanate group.

[0012] In one embodiment of the present invention, the coating material further comprises 1 to 70% by weight of a film forming resin.

[0013] In one embodiment of the present invention, the coating material further comprises 0.5 to 20% by weight of a silicone compound.

5 [0014] In one embodiment of the present invention, a seal layer comprising an inorganic pigment and a film forming resin is provided on the surface of the support.

[0015] In one embodiment of the present invention, the ionizing radiation cured film has a multilayer structure of at least two layers.

10 [0016] In one embodiment of the present invention, in the ionizing radiation cured film having a multilayer structure of at least two layers, 0.5 to 50% by weight of an inorganic pigment is contained in one or at least two layers.

15 [0017] In one embodiment of the present invention, in the ionizing radiation cured film having a multilayer structure of at least two layers, 0.5 to 50% by weight of an inorganic pigment is contained in the lowermost layer.

20 [0018] In one embodiment of the present invention, in the ionizing radiation cured film having a multilayer structure of at least two layers, 0.5 to 20% by weight of a silicone compound is contained in one or at least two layers.

[0019] In one embodiment of the present invention, in the ionizing radiation cured film having a multilayer structure of at least two layers, 0.5 to 20% by weight of a silicone compound is contained in the uppermost layer.

25 [0020] In one embodiment of the present invention, in the ionizing radiation cured film having a multilayer structure of two or more layers, 0.5 to 50% by weight of an inorganic pigment is contained in the lowermost layer, and 0.5 to 20% by weight of a silicone compound is contained in the uppermost layer.

30 [0021] In one embodiment of the present invention, in the ionizing radiation cured film having a multilayer structure of two or more layers, 0.5 to 50% by weight of an inorganic pigment is contained in the lowermost layer, and 0.5 to 20% by weight of a silicone compound is contained in each layer.

35 [0022] In one embodiment of the present invention, the paper as the support is neutral paper.

[0023] In one embodiment of the present invention, the paper as

the support has been embossed.

[0024] According to the another aspect of the present invention, there is provided a process for producing the above embossed release paper for synthetic leather production, characterized by comprising the 5 steps of: coating a coating liquid onto a surface of a support at a coverage of 1 to 40 g/m² on a dry basis to form a coating film; vaporizing the solvent from the coating film to dry the coating film; and applying an ionizing radiation to the coating film to form an ionizing radiation cured film after embossing either the support and the dried 10 coating film simultaneously; wherein the coating material has a softening point of 40°C or above and has been diluted with 10 to 1000 parts by weight of the solvent based on 100 parts by weight on a solid basis of the coating material.

[Effect of Invention]

[0025] According to the invention, there is provided an embossed 15 release paper which has excellent heat resistance and separability from a two-pack curing type adhesive, that is, can be applied in the production of all of synthetic leathers, excellent releasability after repeated use and embossability, and can be obtained at low cost.

[BEST MODE FOR CARRYING OUT THE INVENTION]

[0026] The coating material, which is used in the invention, will be first described.

[0027] The coating material used in the present invention is a composition containing an ionizing radiation curing composition having 25 a softening point of 40°C or above, the ionizing radiation curing composition comprising a product of a reaction of an isocyanate compound with an (meth)acrylic compound containing an (meth)acryloyl group and reactive with the isocyanate compound.

[0028] As used herein, the term "(meth)acryloyl group" refers to an 30 acryloyl group and/or a methacryloyl group, the term "(meth)acrylic compound" refers to an acrylic compound and/or a methacrylic compound, the term "(meth)acrylate" refers to acrylate and/or methacrylate, and the term "(meth)acrylic acid" refers to acrylic acid and/or methacrylic acid.

[0029] The isocyanate compound used in the present invention is a 35 compound containing at least one isocyanate group, preferably a compound containing two or more isocyanate groups. Examples of

such isocyanate compounds include aliphatic isocyanates such as phenyl isocyanate, xylyl isocyanate, naphthyl isocyanate, hexamethylene diisocyanate, lysine methyl ester isocyanate, and 2,4,4-trimethylhexamethylene diisocyanate, alicyclic isocyanates such as isophorone diisocyanate and 4,4'-methylenebis(cyclohexyl isocyanate), aromatic isocyanates such as tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, and naphthalene-1,5'-diisocyanate, and, further, a trimer of tolylene diisocyanate and a product of a reaction between a tolylene diisocyanate and an active hydrogen compound, for example, trimethylolpropane at a ratio of 3 : 1 (molar ratio). Further, for example, compounds containing an isocyanate group attached to a nonaromatic hydrocarbon ring, that is, trimers of the so-called alicyclic isocyanate compounds, or a product of a reaction thereof with an active hydrogen compound are preferred.

Preferably, isophorone diisocyanate, which is easily commercially available, are used as the alicyclic isocyanate compound. Hydrogenated tolylene diisocyanate, hydrogenated xylylene diisocyanate, hydrogenated diphenylmethane diisocyanate and the like may also be used.

[0030] Trimer of isophorone diisocyanate, or a product of a reaction between isophorone diisocyanate and trimethylolpropane (molar ratio 3 : 1) is preferred as the isocyanate compound used in the present invention. The isophorone diisocyanate trimer is further preferred. A plurality of isocyanate compounds may be used in combination.

[0031] An (meth)acrylic compound containing a hydroxyl group and/or a carboxyl group may be mentioned as the (meth)acrylic compound containing an (meth)acryloyl group and reactive with an isocyanate compound. The "(meth)acrylic compound containing an (meth)acryloyl group and reactive with an isocyanate compound" will be hereinafter often referred to as "specific (meth)acrylic compound."

[0032] The product of a reaction between the isocyanate compound and the specific (meth)acrylic compound containing a hydroxyl group is generally called "urethane acrylate." The product of a reaction between the isocyanate compound and the specific (meth)acrylic compound containing a carboxyl group can be brought to a compound having a structure in which a polymerizable (meth)acryloyl group has been attached through an amide group. These will be described.

[0033] A hydroxyl ester, which is a product of a reaction between (meth)acrylic acid and a polyhydroxy compound, may be mentioned as a typical specific (meth)acrylic compound containing a hydroxyl group. Further, a compound prepared by adding ethylene oxide, propylene oxide, caprolactone or the like to the hydroxyl group in the hydroxyl ester may also be mentioned as the specific (meth)acrylic compound containing a hydroxyl group. Further, a compound prepared by esterifying a part of the hydroxyl group in the hydroxy ester with a monocarboxylic acid is also possible.

[0034] Examples of such compounds include hydroxy (meth)acrylates such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, hydroxybutyl (meth)acrylate, trimethylopropane diacrylate, pentaerythritol triacrylate, dipentaerythritol tetraacrylate, and dipentaerythritol pentaacrylate, isocyanuric acid diacrylate, pentaerythritol diacrylate monostearate, 2-hydroxy-3-phenoxypropyl acrylate, and, further, their caprolactone adducts, ethylene oxide adducts, propylene oxide adducts, and ethylene oxide-propylene oxide adducts.

[0035] A hydroxyl group in epoxy acrylate may also be utilized. Specific examples of such compounds include epoxy acrylates produced by reacting acrylic acid with a compound containing two epoxy groups in one molecule, such as neopentyl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether, hydrogenated bisphenol A diglycidyl ether, ethylene glycol diglycidyl ether, or propylene glycol diglycidyl ether. These components contain two (meth)acryloyl groups in one molecule and thus can also function to improve the crosslinking density.

[0036] Specific (meth)acrylic compounds containing a carboxyl group include (meth)acrylic acid per se, and compounds produced by reacting the above hydroxy (meth)acrylate with a carboxylic anhydride, for example, maleic anhydride, succinic anhydride, phthalic anhydride, and tetrahydrophthalic anhydride.

[0037] Some examples of such compounds include pentaerythritol triacrylate succinic acid monoester, dipentaerythritol pentaacrylate succinic acid monoester, pentaerythritol triacrylate maleic acid monoester, dipentaerythritol pentaacrylate maleic acid monoester, pentaerythritol triacrylate phthalic acid monoester, dipentaerythritol triacrylate phthalic acid monoester, pentaerythritol triacrylate

tetrahydrophthalic acid monoester, dipentaerythritol pentacrylate tetrahydrophthalic acid monoester.

[0038] In the reaction of the isocyanate compound with the specific (meth)acrylic compound, other active hydrogen compound reactive with the isocyanate compound may also be used in combination of these compounds. That is, a compound free from an (meth)acryloyl group and reactive with the isocynate group may be used in combination with these compounds.

[0039] When the active hydrogen compound is selected and used in combination with the isocyanate compound and the specific (meth)acrylic compound depending upon the purpose, the softening point of the resultant curable composition is increased, or the flexibility of the final cured coating film is increased. Hydroxyl group-containing compounds are generally used as this active hydrogen-containing compound. Alternatively, for example, amino group-containing compounds and carboxyl group-containing compounds may also be used.

[0040] Hydroxyl group-containing compounds usable herein include polyhydric alcohols containing three or more hydroxyl groups such as glycerin, trimethylolpropane, trimethylolethane, 1,2,6-hexanetriol, 2-hydroxyethyl-1,6-hexanediol, 1,2,4-butanetriol, erythritol, sorbitol, pentaerythritol, and dipentaerythritol; aliphatic glycols such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, 2-methyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 2-methyl-2,4-pantanediol, 1,6-hexanediol, 2-ethyl-1,3-hexanediol, neopentyl glycol, 1,3,5-trimethyl-1,3-pantanediol, 2,2,4-trimethyl-1,3-pantanediol, 1,8-octanediol, 1,9-nanediol, and 2-methyl-1,8-octanediol; alicyclic glycols such as 1,4-cyclohexanediol and 1,4-cyclohexanedimethanol; and aromatic glycols such as xylylene glycol and bishydroxyethoxybenzene.

[0041] Further, high-molecular weight polyols such as polyether polyols, polyester polyols, polyether ester polyols, polycarbonate polyols, and polyacrylic polyols may also be used. Polyether polyols

includes bisphenol A and glycols such as ethylene glycol, propylene glycol, and diethylene glycol, polyols containing three or more hydroxyl groups such as glycerin, trimethylolethane, trimethylolpropane, and pentaerythritol, or polyols produced by addition polymerization of 5 polyamines such as ethylenediamine or toluenediamine and an alkylene oxide such as ethylene oxide or propylene oxide, and polytetramethylene ether glycols produced by ring opening polymerization of tetrahydrofuran.

[0042] Polyester polyols include those produced by a 10 polycondensation reaction of carboxylic acids, for example, dicarboxylic acids such as succinic acid, adipic acid, sebacic acid, azelaic acid, or phthalic acid, or tri- or tetracarboxylic acids such as trimellitic acid or pyromellitic acid, with diols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 15 2,2-diethylpropanediol, 2-ethyl-2-butylpropanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, 1,4-cyclohexanediol, and 1,4-cyclohexanedimethanol, triols such as trimethylolpropane or glycerin, or aromatic polyhydroxy compounds such as bisphenol A or bisphenol F.

[0043] Polyether ester polyols include those produced by reacting 20 polyester glycals with alkylene oxides and those produced by reacting ether group-containing diols or a mixture thereof with other glycol, with the above dicarboxylic acids or their anhydrides, for example, poly(polytetramethylene ether) adipate. Polycarbonate polyols include, 25 for example, those produced by a dealcoholization condensation reaction of polyhydric alcohols with dimethyl, diethyl or other dialkyl carbonates, those produced by a dephenolization condensation reaction of polyhydric alcohols with diphenyl carbonate, and those produced by a deethyleneglycolization condensation reaction of a 30 polyhydric alcohol with ethylene carbonate. Polyhydric alcohols usable in these condensation reactions include, for example, aliphatic diols such as 1,6-hexanediol, diethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 3-methyl-1,5-pentanediol, 2,2-diethylpropanediol, 2-ethyl-2-butylpropanediol, and 35 neopentylglycol, or alicyclic diols such as 1,4-cyclohexanediol and 1,4-cyclohexanedimethanol.

[0044] Amino group-containing compounds (amine compounds)

include hexamethylenediamine, xylylenediamine, isophoronediamine, and N,N-dimethylethylenediamine. Further, amino alcohols such as monoethanolamine and diethanolamine may also be used as the active hydrogen-containing compound.

- 5 [0045] Carboxyl group-containing compounds (organic carboxylic acids) include lauric acid, stearic acid, oleic acid, palmitic acid, adipic acid, sebacic acid, phthalic acid, isophthalic acid, and terephthalic acid.
- [0046] In order to that the properties of a product of a reaction between the isocyanate compound and the specific (meth)acrylic compound are not sacrificed, preferably, these active hydrogen compounds other than the specific (meth)acrylic compound are used so that the molar ratio of the reactive group in the active hydrogen compound to the reactive group in the specific (meth)acrylic compound is not more than 50%, particularly preferably not more than 40%.
- 10 [0047] The reaction of the isocyanate compound with the specific (meth)acrylic compound is preferably carried out in a solvent. The use of the solvent is advantageous in that the reaction can easily be controlled, and the viscosity of the reaction product can be regulated. Solvents usable herein include inert solvents commonly used in this type of reaction, for example, aromatic hydrocarbon solvents such as toluene and xylene, ketone solvents such as methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone, ester solvents such as ethyl acetate, butyl acetate, and isobutyl acetate, glycol ether ester solvents such as diethylene glycol ethyl ether acetate, propylene glycol methyl ether acetate, 3-methyl-3-methoxybutyl acetate, and ethyl-3-ethoxypropionate, ether solvents such as tetrahydrofuran and dioxane, and aprotic polar solvents such as N-methylpyrrolidone.
- 15 [0048] In the reaction, reaction starting materials may be added to a solvent so that the concentration of the reaction product in the solution after the reaction is 30 to 80% by weight, followed by a reaction at 50 to 80°C optionally in the presence of 0.01 to 0.1% by weight, based on the reaction starting materials, of an organotin catalyst. The charge ratio between the isocyanate compound and the specific (meth)acrylic compound and optionally used other active hydrogen compound is preferably that, based on one mole of the isocyanate group in the isocyanate compound, the amount of the functional group in the specific (meth)acrylic compound and other
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- 25
- 30
- 35

active hydrogen compound reactive with the isocyanate compound is not less than 0.5 mole, particularly preferably not less than 1 mole. The reaction time is generally about 3 to 8 hr. Preferably, however, the reaction is stopped at the time when, in the trace of the content of the isocyanate group in the reaction solution by analysis, the content of the isocyanate group reached a target value.

[0049] The ionizing radiation curing composition according to the present invention is a product of a reaction between the isocyanate compound and the specific (meth)acrylic compound and has a softening point of 40°C or above. The softening point of the ionizing radiation curing composition is preferably 50°C or above, more preferably 60°C or above. When the softening point of the ionizing radiation curing composition is below 40°C, blocking occurs in the coating film before curing, or the embossability is poor.

[0050] The softening point specified in the present invention refers to a softening point of a residue obtained by removing the solvent from the reaction product as measured under the following conditions.

[0051]

-Measuring apparatus: ARES-2KFRTNI, manufactured by Rheometrics Corp.,

-Measuring mode: Test on temperature dependency of dynamic viscoelasticity, 25-mm parallel plate,

-Measuring temperature range: -50 to 150°C, and

-Vibration frequency: 1 rad/sec.

In the measurement under the above conditions, the temperature at which the melt viscosity is 5000 Pa·sec, is defined as the softening point.

[0052] The content of the (meth)acryl group in the ionizing radiation curing composition according to the present invention is preferably not less than 5% by weight, more preferably not less than 10% by weight, as calculated on the premise that the molecular weight of the olefinic double bond (-C=C-) is 24. When the content of the (meth)acryl group is low, the crosslinking density after curing by ionizing radiation irradiation is lowered. Consequently, the solvent resistance, heat resistance and the like are unsatisfactory, and unfavorable phenomena such as poor separation and shaping sag occurs in polyvinyl chloride film formation.

[0053] The content of the olefinic double bond is measured by IR, NMR or the like. When the production process is known, the content of the olefinic double bond can also be determined by calculation based on the charging amount of the starting material.

5 [0054] The coating material used in the present invention may contain, in addition to the silicone compound, optionally a film forming resin, an inorganic pigment and the like for modifying curing properties of the reaction product.

10 [0055] Film forming resins usable herein include methacrylic resins, chlorinated polypropylene, epoxy resins, polyurethane resins, polyester resins, polyvinyl alcohols, and polyvinylacetals. These film forming resins may or may not contain a reactive group. Reactive groups include (meth)acryloyl, vinyl, amino, mercapto, epoxy, carboxyl, phenol, and hydroxyl groups. Methacrylic resins are preferred, for 15 example, from the viewpoints of adhesion to the base material and film forming properties. Methacrylic resins having a glass transition temperature (T_g) of 40°C or above are preferred from the viewpoint of embossability. A T_g value of 50°C or above is further preferred. In addition to conventional methacrylic compounds, for example, maleic 20 anhydride, methacrylic acid, styrene, hydroxyethyl methacrylate, maleimide group-containing methacrylate, and isobornyl group-containing methacrylate may be used as the comonomer component.

25 [0056] The amount of the resin having film forming properties used is generally not more than 70% by weight, preferably 1 to 70% by weight, more preferably 20 to 60% by weight, in terms of the content of the resin in the coating liquid. When the amount of the resin exceeds 70% by weight, that is, when the amount of the ionizing radiation curing composition is less than 30% by weight, the heat resistance after 30 curing by ionizing radiation irradiation is unsatisfactory. The incorporation of a suitable amount of the film forming resin has the effect of improving the adhesion to the base material, film forming properties and the like.

35 [0057] The silicone compound used in the present invention may be reactive or nonreactive. Reactive silicone compounds include (meth)acryloyl modified, vinyl modified, amino modified, mercapto modified, epoxy modified, carboxyl modified, phenol modified, and

alcohol modified silicone compounds.

[0058] More specific examples of reactive silicone compounds include (meth)acryloyl modified silicones such as X-22-164B and X-22-164C (manufactured by The Shin-Etsu Chemical Co., Ltd.) and FM-0711, FM-0721, and FM0725 (manufactured by Chisso Corp.), vinyl modified silicones such as XF40-A1987 (manufactured by Toshiba Silicone Co., Ltd.), amino modified silicones such as TSF4700, TSF4702, and TSF4705 (manufactured by Toshiba Silicone Co., Ltd.), X-22-161AS, KF393, and KF864 (manufactured by The Shin-Etsu Chemical Co., Ltd.), and BY16-208 and SF8417 (manufactured by Dow Corning Toray Silicone Co., Ltd.), mercapto modified silicones such as X-22-167B and KF-2001 (manufactured by The Shin-Etsu Chemical Co., Ltd.), epoxy modified silicones such as YF3965 and TSF4730 (manufactured by Toshiba Silicone Co., Ltd.), KF105 and X-22-169AS (manufactured by The Shin-Etsu Chemical Co., Ltd.), and SF8421 and SF8413 (manufactured by Dow Corning Toray Silicone Co., Ltd.), carboxy modified silicones such as TSF4770 and XF-A9248 (manufactured by Toshiba Silicone Co., Ltd.), X-22-162A and X-22-3701E (manufactured by The Shin-Etsu Chemical Co., Ltd.), and SF8418 and BY-16-750 (manufactured by Dow Corning Toray Silicone Co., Ltd.), phenol modified silicones such as X-22-165B (manufactured by The Shin-Etsu Chemical Co., Ltd.), and BY16-752 and BY16-150C (manufactured by Dow Corning Toray Silicone Co., Ltd.), and alcohol modified silicones such as TSF4750 and TSF4751 (manufactured by Toshiba Silicone Co., Ltd.), BY16-848 and BY16-201 (manufactured by Dow Corning Toray Silicone Co., Ltd.) and FM-4411, FM-4425, FM-0411, FM-0425 and FM-DA21 (manufactured by Chisso Corp.).

[0059] Further, silicone compounds synthesized using these reactive silicones may be used. A reactive group may be present or absent in the synthesized silicone compound. Silicone compounds synthesized using the reactive silicone include silicone modified (meth)acrylic polymers and silicone modified (meth)acrylates using (meth)acryloyl modified silicones; silicone modified epoxy acrylates using epoxy modified silicones; and silicone modified urethane polymers and silicone modified urethane acrylates using alcohol modified silicones. Among them, silicone modified urethane acrylates are particularly preferred.

[0060] Nonreactive silicone compounds include reactive group-free silicone compounds as described above. Specific examples of such compounds include dimethylpolysiloxanes such as TSF451 and YF3800 (manufactured by Toshiba Silicone Co., Ltd.), KF96A (manufactured by
5 The Shin-Etsu Chemical Co., Ltd.), and SH200 (manufactured by Dow Corning Toray Silicone Co., Ltd.); methylphenylpolysiloxanes such as TSF433 and TSF434 (manufactured by Toshiba Silicone Co., Ltd.) and SH510 and SH702 (manufactured by Dow Corning Toray Silicone Co., Ltd.); and polyether modified silicones such as TSF4440 and TSF 4445
10 (manufactured by Toshiba Silicone Co., Ltd.), KF-351 and KF-353 (manufactured by The Shin-Etsu Chemical Co., Ltd.), SH3746 and SH3748 (manufactured by Dow Corning Toray Silicone Co., Ltd.) and SS-2803 and SS-2801 (manufactured by Nippon Unicar Co., Ltd.).

[0061] These silicone compounds may be used solely or in a combination of two or more. Both the reactive and nonreactive silicone compounds may also be used. From the viewpoint of compatibility with other component and the like, preferably, the silicone compound has a ring structure such as an aromatic, alicyclic or isocyanuric acid skeleton. Silicone compounds having a ring structure include silicone compounds with a phenyl group introduced into the side chain such as methylphenylsilicone and silicones produced by introducing a ring structure using a reactive silicone. Silicones produced by introducing a ring structure using a reactive silicone include silicone compounds containing a phenyl group introduced by
20 copolymerizing (meth)acryloyl modified silicones with styrene, and silicone compounds produced by introducing a ring structure into a silicone modified urethane polymer or a silicone modified urethane acrylate, for example, using a monomer or trimer of diphenylmethane diisocyanate, naphthalene diisocyanate, or isophorone diisocyanate.
25 A reactive group may be present or absent in these silicone compounds having a ring structure.

[0062] The content of the silicone compound in a coating material containing the ionizing radiation curing composition is not more than 20% by weight, preferably 0.5 to 20% by weight, more preferably 1 to
30 15% by weight. When the content of the silicone compound is larger than 20% by weight, the coating film is tacky or the cost is high. On the other hand, when the content of the silicone compound is less than

0.5% by weight, the effect of improving the separability is unsatisfactory.

[0063] Further, the coating liquid may contain, in addition to or instead of the above film forming resin and silicone compound, for example, reactive monomers, reactive oligomers, pigments, photopolymerization initiators, polymerization inhibitors, colorants, and surfactants.

[0064] Preferred reactive monomers include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, ethylhexyl (meth)acrylate, stearyl (meth)acrylate, lauryl (meth)acrylate, tridecyl (meth)acrylate, trimethylolpropane triacrylate, tris(acryloxyethyl) isocyanurate, pentaerythritol tetraacrylate, and dipentaerythritol hexaacrylate.

[0065] Preferred reactive oligomers include epoxy acrylate, urethane acrylate, polyester acrylate, and polyether acrylate.

[0066] Photopolymerization initiators usable herein include benzoin ethyl ether, acetophenone, diethoxyacetophenone, benzyl dimethyl ketal, 2-hydroxy-2-methylpropiophenone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1,1-hydroxycyclohexyl phenyl ketone, benzophenone, p-chlorobenzophenone, Michler's ketone, isoamyl N,N-dimethylaminobenzoate, 2-chlorothioxanthone, and 2,4-diethylthioxanthone.

[0066] Photopolymerization initiators usable herein include benzoin ethyl ether, acetophenone, diethoxyacetophenone, benzyl dimethyl ketal, 2-hydroxy-2-methylpropiophenone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropane-1,1-hydroxycyclohexyl phenyl ketone, benzophenone, p-chlorobenzophenone, Michler's ketone, isoamyl N,N-dimethylaminobenzoate, 2-chlorothioxanthone, and 2,4-diethylthioxanthone.

[0067] A solvent may be properly added to give a viscosity suitable for coating, followed by coating. Solvents usable herein include, for example, aromatic hydrocarbon solvents such as toluene and xylene, ketone solvents such as methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone, ester solvents such as ethyl acetate, butyl acetate, and isobutyl acetate, glycol ether ester solvents such as diethylene glycol ethyl ether acetate, propylene glycol methyl ether acetate, propylene glycol monomethyl ether, 3-methyl-3-methoxybutyl acetate,

and ethyl-3-ethoxypropionate, ether solvents such as tetrahydrofuran and dioxane, and aprotic polar solvents such as N-methylpyrrolidone.

[0068] Next, the support used in the invention will be first described.

For example, noncoated papers such as wood free paper, kraft paper,

5 machine glazed kraft paper, pure white machine glazed paper, glassine paper, and cup base paper, and, further, coated papers such as inorganic pigment layer-coated art paper, coated paper, and cast coated paper, and synthetic papers not using natural pulp may be used as the support. When the use of the release paper particularly in the production of PVC leathers is contemplated, the use of neutral paper rather than acidic paper is preferred because heat resistance high enough to withstand embossing at a high temperature of 200°C or above is required. In the acidic paper, rosin sizing agents using aluminum sulfate as a fixing agent are used as the sizing agent. On 10 the other hand, in the neutral paper, neutral sizing agents, not using aluminum sulfate as the fixing agent, for example, neutral rosin sizing agents, alkeylketene diamers (AKDs), and alkenylsuccinic anhydrides (ASA), are used.

[0069] Further, satisfactory strength, and proper smoothness, preferably, the pulp is a mixture composed of a softwood pulp and a hardwood pulp and having a softwood pulp content of not less than 20% and has a basis weight of 80 to 250 g/m².

[0070] Preferably, a seal layer formed of the above-described film forming resin or the film forming resin containing an inorganic pigment is provided on the support. The provision of the seal layer can suppress the formation of pinholes derived from the penetration of the coating liquid and further can impart smoothness.

[0071] Film forming resins usable for seal layer formation include polyvinyl alcohols, acrylic resins, styrene-acryl resins, cellulose derivatives, polyester resins, polyurethane resins, melamine resins, alkyd resins, aminoalkyd resins, polyvinyl chloride resins, and polyvinylidene chloride resins. The may be used solely or as a mixture of two or more.

[0072] Inorganic pigments which may be added to the resin include talc, kaolin, silica, calcium carbonate, barium sulfate, titanium oxide, and zinc oxide. The pigment is generally incorporated in an amount of 0.5 to 70% by weight based on the film forming resin. The coverage of

the seal layer may be 0.5 to 20 g/m². When the coverage is below the lower limit of the above-defined range, the seal effect cannot be attained. On the other hand, when the coverage is above the upper limit of the above-defined range, the embossability is deteriorated.

5 The sealing material may be coated in the same manner as in the coating liquid containing the ionizing radiation curing resin composition.

[0073] The coating material, which form the ionizing radiation cured film may be used after dilution generally with 10 to 1000 parts by weight of a solvent based on 100 parts by weight of the solid content.

10 Dilution with the solvent can impart a proper viscosity, for example, a viscosity of 10 to 3000 mPa·sec at 25°C, to the coating liquid and, at the same time, in the step of drying the coating, can realize proper transfer of the silicone compound onto the surface.

[0074] The coating liquid may be coated by conventional methods such as direct gravure coating, reverse gravure coating, gravure offset coating, microgravue coating, direct roll coating, reverse roll coating, curtain coating, knife coating, air knife coating, bar coating, die coating, and spray coating. After coating onto a paper base material, the solvent is evaporated in a drying oven to form a coating film.

20 [0075] Good embossability can be provided by coating the coating liquid at a coverage of 1 to 40 g/m², preferably 5 to 20 g/m² on a dry weight basis after the evaporation of the solvent.

[0076] The ionizing radiation cured film layer preferably has a multilayer structure of two or more layers. The adoption of the multilayer structure can further reduce the occurrence of pinholes. When the ionizing radiation cured film layer has a multilayer structure of two or more layers, preferably, the lowermost layer in the multilayer structure contains 0.5 to 50% by weight, particularly preferably 1 to 10% by weight, of an inorganic pigment. Suitable inorganic pigments usable herein include talc, kaolin, silica, calcium carbonate, barium sulfate, titanium oxide, and zinc oxide. Further, the silicone compound may be contained only in the uppermost layer in the two or more layers constituting the ionizing radiation cured film layer, or alternatively may be contained in each of the layers.

35 [0077] The coating liquid is coated onto a support. Since the dried coating film is tack-free, after drying, the assembly including the paper base material may be wound without causing blocking. Embossing as

post processing may be carried out offline. Good embossing without causing deposition of the coating liquid onto an emboss roll can be realized by properly setting the temperature of the emboss roll and the softening temperature of the coating liquid.

5 [0078] Embossing is generally carried out by transfer with a metal emboss roll having a concave-convex pattern for emboss formation. Alternatively, a belt-type or flat plate-type press may be used. When the emboss roll is used, both-side emboss in which a male die is provided in the emboss roll while a female die is provided in a backup roll, or one-side emboss in which concaves and convexes are not provided in the backup roll, may be used.

10 [0079] When the support with the coating liquid coated thereon is embossed from the top of the coating by using the above embossing device, the support is heated so that the temperature of the coating liquid is brought to 50 to 150°C. Preferably, this temperature is above the softening point of the ionizing radiation curing composition contained in the coating liquid and below the melting temperature of the resin. The heating is generally carried out by heating the roll per se, for example, by passing steam through the emboss roll.

15 [0080] Alternatively, a preheating method may also be adopted in which the coating liquid is heated just before embossing.

20 [0081] In order to realize good tack-free properties and embossability, as described above, the softening point of the ionizing radiation curing composition is 40°C or above, preferably 50°C or above.

25 [0082] When the softening point is below 40°C, the tack-free properties and embossability are unsatisfactory.

30 [0083] After embossing, ultraviolet light or electron beam is applied from the curable coating film side to cure the curable coating film formed by coating the coating liquid. Ultraviolet light sources usable herein include low pressure mercury lamps, medium pressure mercury lamps, high pressure mercury lamps, metal halide lamps, xenon lamps, and tungsten lamps. Electron beam irradiation methods include scanning methods, curtain beam methods, and broad beam methods, and 50 to 300 kV is suitable as the acceleration voltage of the electron beam.

35 [0084] Fig. 1 is a diagram showing an embodiment of a production process of a release paper according to the present invention. In the

drawing, numeral 1 designates a leading roll, numeral 2 an emboss roll, numeral 3 a backup roll, numeral 4 a winding roll, numeral 5 a paper with curable coating film, numeral 6 paper with an embossed curable coating film, and numeral 7 an embossed release paper. Character A 5 designates the step of embossing, and character B the step of ionizing radiation irradiation.

[0083] Next, a process for producing a synthetic leather, by using the release paper obtained in the invention, will be first described. The synthetic leather may be obtained by conventional methods. For 10 example, a PU leather has been produced by coating a PU resin paste for a skin layer onto a release paper, drying and solidifying the coating at a temperature of 90 to 140°C, applying the assembly to a backing fabric with the aid of a two-component curing type PU-based adhesive, allowing a reaction to proceed in a curing room of 40 to 70°C for 2 to 3 15 days, and peeling off the release paper. Further, a PVC leather has been produced, for example, by coating a PVC sol onto a release paper, heating the coating to cause gelation, then forming a PVC expanded layer, applying the assembly to a backing fabric, and then peeling off the release paper.

20 [EXAMPLES]

[0084] The following Examples further illustrate the present invention. However, it should be noted that the present invention is not limited to these Examples, and various modifications and changes may be made within the scope of the present invention.

25 [0085] Synthesis of ionizing radiation curing composition A:

Ethyl acetate (206.1 g) and 133.5 g of a trimer of isophorone diisocyanate (VESTANAT T1890, manufactured by Degussa) were charged into a reactor equipped with a stirrer, a reflux condenser, a dropping funnel, and a thermometer and were heated to 80°C for 30 dissolution. After air was blown into the solution, 0.38 g of hydroquinone monomethyl ether, 249.3 g of a mixture composed of pentaerythritol triacrylate and pentaerythritol tetraacrylate (Viscoat 300, manufactured by Osaka Organic Chemical Industry Ltd.), and 0.38 g of dibutyltin dilaurate were charged into the reactor. A reaction was 35 allowed to proceed at 80°C for 5 hr, 688.9 g of ethyl acetate was then added, and the mixture was cooled. The resultant reaction product solution was analyzed by infrared absorption spectroscopy. As a result,

it was confirmed that absorption attributable to an isocyanate group disappeared. Ethyl acetate was removed from the reaction product solution by evaporation, and the softening point of the residue was measured and was found to be 43°C.

5 [0086] Synthesis of ionizing radiation curing composition B:

Methyl ethyl ketone (256.67 g) and 110 g of a trimer of isophorone diisocyanate were charged into a reactor equipped with a stirrer, a reflux condenser, a dropping funnel, and a thermometer and were heated to 80°C for dissolution. After air was blown into the 10 solution, 0.30 g of hydroquinone monomethyl ether, 381.2 g of a mixture composed of dipentaerythritol hexaacrylate and dipentaerythritol pentaacrylate (KAYARAD DPHA, manufactured by Nippon Kayaku Co., Ltd.), 21.2 g of 1,4-butanediol, and 0.30 g of dibutyltin dilaurate were charged into the reactor. A reaction was 15 allowed to proceed at 80°C for 5 hr, 939.02 g of methyl ethyl ketone was added thereto, and the mixture was cooled. The resultant reaction product solution was analyzed by infrared absorption spectroscopy. As a result, it was confirmed that absorption attributable to an isocyanate group disappeared. Methyl ethyl ketone was removed from the 20 reaction product solution by evaporation, and the softening point of the residue was measured and was found to be 42°C.

[0087] Synthesis of ionizing radiation curing composition C:

Methyl ethyl ketone (256.67 g) and 110 g of a trimer of isophorone diisocyanate were charged into a reactor equipped with a stirrer, a reflux condenser, a dropping funnel, and a thermometer and were heated to 80°C for dissolution. After air was blown into the 25 solution, 0.20 g of hydroquinone monomethyl ether, 146.65 g of a mixture composed of pentaerythritol tetraacrylate and pentaerythritol triacrylate, 30.08 g of epoxy acrylate (Epoxy Ester 70PA, manufactured by Kyoeisha Chemical Co., Ltd.), and 0.20 g of dibutyltin dilaurate were charged into the reactor. A reaction was allowed to proceed at 80°C for 30 5 hr, 412.37 g of methyl ethyl ketone was then added, and the mixture was cooled. The resultant reaction product solution was analyzed by infrared absorption spectroscopy. As a result, it was confirmed that 35 absorption attributable to an isocyanate group disappeared. Methyl ethyl ketone was removed from the reaction product solution by evaporation, and the softening point of the residue was measured and

was found to be 68°C.

[0088] Synthesis of ionizing radiation curing composition D;

Methyl ethyl ketone (256.67 g) and 110 g of isophorone diisocyanate (VESTANAT IPDI, manufactured by Degussa) were charged into a reactor equipped with a stirrer, a reflux condenser, a dropping funnel, and a thermometer and were heated to 80°C for dissolution. After air was blown into the solution, 0.40 g of hydroquinone monomethyl ether, 448.53 g of a mixture composed of pentaerythritol tetraacrylate and pentaerythritol triacrylate, and 0.40 g of dibutyltin dilaurate were charged into the reactor. A reaction was allowed to proceed at 80°C for 5 hr, 1046.57 g of methyl ethyl ketone was then added, and the mixture was cooled. The resultant reaction product solution was analyzed by infrared absorption spectroscopy. As a result, it was confirmed that absorption attributable to an isocyanate group disappeared. Methyl ethyl ketone was removed from the reaction product solution by evaporation. As a result, the residue was a viscous liquid, and, thus, the softening temperature was immeasurable.

[0089] Procurement of ionizing radiation curing composition E;

A mixture composed of dipentaerythritol hexaacrylate and dipentaerythritol pentaacrylate (KAYARAD DPHA, manufactured by Nippon Kayaku Co., Ltd.) as such was used.

[0090] Preparation of film forming resin (a);

A solution of 30 g of isobornyl methacrylate, 65 g of methyl methacrylate, and 5 g of glycidyl methacrylate dissolved in 200 g of toluene was heated in a reactor equipped with a stirrer, a reflux condenser, a dropping funnel, and a thermometer to 65°C. When the temperature reached 65°C, 0.5 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was added to the solution. Further, two hr after the temperature reached 65°C, 0.5 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was again added to the solution. A reaction was allowed to proceed at 65°C for additional 5 hr to give a copolymer. Thereafter, while blowing air into the solution, the temperature of the solution was intermittently raised to 108°C. Hydroquinone monomethyl ether (0.2 g) and 0.2 g of triphenylphosphine were added thereto, 2.5 g of acrylic acid was then added, and a reaction was allowed to proceed for 5 hr to give an acryloyl

group-containing film forming resin.

[0091] Preparation of film forming resin (b);

4-Hydroxyethyl methacrylate (5 g), 20 g of isobornyl methacrylate, 75 g of methyl methacrylate, 200 g of methyl ethyl ketone, and 0.5 g of 2,2'-azobis(2,4-dimethylvaleronitrile) were placed in a reactor equipped with a stirrer, a reflux condenser, a dropping funnel and a thermometer, followed by polymerization at 65°C for 6 hr. Thereafter, air was blown into the solution, and 0.2 g of hydroquinone monomethyl ether and 0.2 g of dibutyltin dilaurate were added thereto. An isocyanate group-containing acrylate (VI-1 manufactured by KAGAWA CHEMICAL LTD.) (10.7 g) was then added, the mixture was then heated to 80°C, and a reaction was allowed to proceed for 5 hr to give an acryloyl group-containing film forming resin.

[0092] Preparation of film forming resin (c);

A commercially available product of a methacrylic ester resin (PARAPET GF, manufactured by Kuraray Co., Ltd.) as such was used.

[0093] Synthesis of silicone compound (α);

Methyl ethyl ketone (23.3 g), 10 g of isophorone diisocyanate, 20.4 g of a mixture composed of pentaerythritol tetraacrylate and pentaerythritol triacrylate, 0.10 g of dibutyltin dilaurate, and 0.10 g of hydroquinone monomethyl ether were charged into a reactor equipped with a stirrer, a reflux condenser, a dropping funnel, and a thermometer. Air was blown into the solution, and a reaction was then allowed to proceed at 25°C for 3 hr. Thereafter, while intermittently raising the temperature to 80°C, a reaction was allowed to proceed for 5 hr. An alcohol modified silicone (FMDA21, manufactured by Chisso Corp.) (240.8 g) was added to the reaction product, and a reaction was further allowed to proceed for 5 hr. Methyl ethyl ketone (609.3 g) was then added, and the mixture was cooled to give a silicone modified urethane acrylate containing an acryloyl group and a silicone.

[0094] Synthesis of silicone compound (β);

A solution of 10 g of 2-hydroxyethyl methacrylate, 40 g of styrene, 40 g of methacryl modified silicone (FM0711, manufactured by Chisso Corp.), and 2 g of laurylmercaptane, dissolved in 200 g of methyl ethyl ketone was heated in a reactor equipped with a stirrer, a reflux condenser, a dropping funnel, and a thermometer to 65°C.

When the temperature reached 65°C, 0.6 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was added to the solution. Further, two hr after the temperature reached 65°C, 0.6 g of 2,2'-azobis(2,4-dimethylvaleronitrile) was again added to the solution.

5 A reaction was allowed to proceed at 65°C for additional 5 hr to give a copolymer. An adduct (79.3 g) prepared by reacting 22.2 g of isophorone diisocyanate with 57.1 g of a mixture composed of pentaerythritol triacrylate and pentaerythritol tetraacrylate at 25°C for 3 hr and then allowing a reaction to proceed for 5 hr while 10 intermittently raising the temperature to 80°C was added to the copolymer, and the mixture was allowed to react at 80°C for 5 hr to give a copolymer containing an acryloyl group and a silicone.

[0095] Synthesis of silicone compound (χ);

A commercially available product of a polyether modified 15 silicone (SS-2803, manufactured by Nippon Unicar Co., Ltd.) as such was used.

[0096] < Pretreatment of support >

20 A neutral paper having a basis weight of 125 g/m² was provided as a support. A silica-containing acrylic resin having the following composition was bar coated as a covering material for a seal layer onto the support at a coverage of 5 g/m² on a dry basis. The coating was dried at 110°C for one min.

[0097] [Acrylic resin]

Styrene-acryl emulsion (X-436 manufactured by 25 SEIKO POLYMER CORPORATION)	25 pts.wt.
Water soluble acrylic resin (PDX-6102, manufactured by Johnson Polymer Corp.)	25 pts.wt.
Silica (SYLYSIA 350, manufactured by Fuji Sylysia Chemical Ltd.)	10 pts.wt.
Isopropyl alcohol	25 pts.wt.
Water	25 pts.wt.

[0098] < Preparation of coating material composition 1 >

The above ionizing radiation curing composition A (30 parts by weight), 60 parts by weight of a film forming resin b, and 10 parts by 35 weight of a silicone compound α (the above "parts by weight" being parts by weight on a solid basis) were mixed together to prepare composition 1. A part of the composition was sampled, and the

softening point thereof was measured and was found to be 76°C.

[0099] < Preparation of coating material compositions 2-9 >

Compositions 2 to 9 were prepared by mixing according to the formulations (parts by weight on a solid basis) shown in Table 1 in the same manner as described above. Silica (SYLYSIA 350 manufactured by Fuji Sylisia Chemical Ltd.) was used as the inorganic pigment. A part of the composition was sampled, and the softening point thereof was measured. The results are also shown in Table 1.

[0100] < Example 1 >

A photopolymerization initiator (Irgacure 907 manufactured by Ciba Specialty Chemicals, K.K.) (3 parts by weight) and methyl ethyl ketone as a diluting solvent were added to composition 1 (100 parts by weight on a solid basis) so that the solid content was 30% by weight. The mixture thus obtained was bar coated onto a neutral paper not provided with a seal layer at a coverage of about 5 to 10 g/m² on a dry basis, and the coating was heat dried at 110°C for one min. Thereafter, the surface of the coating film was embossed. The embossing was carried out by pressing using a combination of a metal emboss roll having a concave-convex pattern and a paper roll as a backup roll with a female die.

[0101] For a particular part (3 mm x 3 mm) in this emboss roll, irregularities (concaves and convexes) were measured with a three-dimensional surface roughness tester (Surfcom 590A, manufactured by Tokyo Seimitsu Co., Ltd.). As a result, average height from center plane (Ra) was 12.99 μm, and ten-point mean roughness (Rz) was 65.78 μm.

[0102] In this case, the temperature of the emboss roll was brought to 120°C, and the support and the dried coating film were simultaneously embossed to satisfactorily emboss a part ranging from the dried coating film face to the backside of the support. It was confirmed that the concave-convex shape was satisfactorily provided in a part ranging from the coating face to the backside of the paper. Next, the coating film was irradiated with ultraviolet light from a high-pressure mercury lamp (output 120 W/cm) at 600 mj/cm² to cure the coating film. Thus, release paper was prepared. For release papers of the Examples, embossability, heat resistance, and separability were measured. The results were demonstrated as shown

in Table 2 below.

[0103] < Examples 2-6 >

In the same manner as described above, each composition shown in the column of "1st layer" in Table 2 below was coated onto a support (a neutral paper provided or not provided with a seal layer) shown in Table 2, and the coating was dried. After drying, in the same manner as described above, each composition shown in the column of "2nd layer" in Table 2 was coated, and the coating was dried. Thereafter, the assembly was embossed in the same manner as described above.

[0104] < Comparative Examples 1-3 >

In the same manner as Example 1, each composition shown in the column of "1st layer" in Table 2 below was coated onto a support (a neutral paper provided with a seal layer) shown in Table 2, and the coating was dried. After drying, in the same manner as described above, each composition shown in the column of "2nd layer" in Table 2 was coated, and the coating was dried. Thereafter, the assembly was embossed in the same manner as described above.

[0105] <Embossability>

Concaves and convexes in the release paper with embosses corresponding to the emboss roll in its particular part being formed were measured with a three-dimensional surface roughness tester. The results were evaluated according to the following criteria.

[0106]

25 ◎ : Both Ra and Rz values were not less than 85% relative to the values of the emboss roll.

○ : Both Ra and Rz values were not less than 70% relative to the values of the emboss roll, and any one of the Ra and Rz values was not less than 85% relative to the value of the emboss roll.

30 △ : Both Ra and Rz values were not less than 70% and less than 85% relative to the values of the emboss roll.

X : Any one of the Ra and Rz values was less than 70% relative to the value of the emboss roll.

[0107] <Production of PVC leather>

5 A vinyl chloride sol having the following composition was bar coated onto the surface of the release paper prepared above at a coverage of 100 g/m², and the coating was heat cured at 220°C for 3 min to form a leather sheet which was then separated from the release paper.

[0108]

Polyvinyl chloride (paste resin)	100 pts.wt.
Diethyl phthalate	60 pts.wt.
Expanding agent (azodicarbonamide)	3 pts.wt.
10 Antioxidant (KF-80A-8, manufactured by Kyodo Chemical Co., Ltd.)	3 pts.wt.
Calcium carbonate 10 pts.wt.	

[0109] <Heat resistance>

15 The above procedure consisting of forming a leather sheet and separating the leather sheet from the release paper was repeated five times. Thereafter, the release paper was inspected for losing of the shape and a deterioration in support. The results were evaluated according to the following criteria.

20 ○ : No losing of shape was observed at the time of the completion of the repetition of the procedure by five times.

△ : Due to losing of shape or surface change of the release paper, the release paper could not be used before the repetition of the procedure by five times.

25 X : The procedure was carried out only once due to losing of shape or breaking caused by a deterioration in support.

[0110] <Cyclic separability>

30 One-component curing-type polyurethane having the following composition was bar coated onto the surface of the release paper prepared above at a coverage of 20 g/m² on a dry basis, and the coating was heat dried at 120°C for 2 min.

[One-component curing-type polyurethane]

Main agent (CRISVON, 7367SL, manufactured by Dainippon Ink and Chemicals, Inc.)	100 pts.wt.
Color (DAILAC, TV-COLOR, manufactured by Dainippon Ink and Chemicals, Inc.)	15 pts.wt.

Solvent (methyl ethyl ketone)	30 pts.wt.
Solvent (dimethylformamide)	10 pts.wt.

Subsequently, a two-component curing-type urethane adhesive having the following composition was bar coated at a coverage of 20 g/m² on a dry basis, and buckskin was applied onto the coating, and the assembly was heated at 120°C for 2 min for heat curing the adhesive, followed by aging at 50°C for 24 hr to prepare a PU leather sheet.

[Two-component curing-type urethane adhesive]

10	Main agent (CRISVON, 4070, manufactured by Dainippon Ink and Chemicals, Inc.)	100 pts.wt.
10	Curing agent (CRISVON, NX, manufactured by Dainippon Ink and Chemicals, Inc.)	50 pts.wt.
15	Accelerating agent (CRISVON, ACCEL, HM manufactured by Dainippon Ink and Chemicals, Inc.)	3 pts.wt.
	Solvent (toluene)	80 pts.wt.
	Solvent (ethyl acetate)	40 pts.wt.

For the PU leather sheet thus obtained, 15 mm width of the leather sheet was separated by 180 degree from the release paper by a tensile tester (TENSILON RTC-1310A, manufactured by Orientec Co., Ltd.) at a rate of 300 mm/min to measure the peel strength. This procedure was repeated five times, and the separability was evaluated according to the following criteria.

25 [0111]

◎ : In the repetition of the procedure by five times, the peel strength was less than 1 N, and the separability substantially remained unchanged.

○ : In the repetition of the procedure by five times, although the separation was possible, the peel strength was increased to not less than 1 N, that is, the separability was somewhat deteriorated.

△ : The separability was considerably deteriorated, and the separation became impossible before the fifth repetition of the

procedure.

X : In the first procedure, the leather sheet could not be successfully separated.

The results were as shown in Table 2 below.

[0112]

[Table 1]

Composition	Ionizing radiation curing composition					Coating liquid (pls.wt. on solid basis)			Silicone compound (inorganic matter content)			Softening temp. of coating liquid, °C
	A	B	C	D	E	a	b	c	α	β	γ	
1	30	-	-	-	-	-	60	-	10	-	-	76
2	-	-	40	-	-	-	-	50	10	-	-	87
3	-	35	-	-	-	60	-	-	-	5	-	80
4	-	-	80	-	-	-	10	-	10	-	-	75
5	60	-	-	-	-	30	-	-	-	-	10	-
6	50	-	-	-	-	-	-	30	-	10	-	64
7	-	-	-	-	70	-	20	-	10	-	-	58
8	-	-	-	40	-	-	-	50	10	-	-	35
9	-	-	-	-	20	-	-	70	-	-	10	40
												68

[0113]

[Table 2]

	Construction of release paper			Embossability	Heat resistance	(Cyclic) separation
	Support	Seal layer	Coating layer			
		1st layer	2nd layer			
Example 1	Neutralized paper	Not provided	Composition 1	-	△	△
Example 2	Neutralized paper	Not provided	Composition 5	○	△	○
Example 3	Neutralized paper	Not provided	Composition 2	△	○	○
Example 4	Neutralized paper	Not provided	Composition 6	○	○	△
Example 5	Neutralized paper	Provided	Composition 5	○	○	○
Example 6	Neutralized paper	Provided	Composition 1	○	△	○
Comparative Example 1	Neutralized paper	Provided	Composition 7	○	○	○
Comparative Example 2	Neutralized paper	Provided	Composition 5	○	x	○
Comparative Example 3	Neutralized paper	Provided	Composition 9	△	x	△

[0114] It is clear from Tables 1 and 2 that:

(1) For Examples 1 to 6, all of the embossability, heat resistance, and cyclic separability are good,

5 (2) For Comparative Example 1, the embossability is poor due to the low softening temperature of the coating material,

(3) For Comparative Example 2 using no ionizing radiation curing composition according to the invention, the embossability is poor, and

10 (4) For Comparative Example 3 using no ionizing radiation curing composition according to the invention, the heat resistance is poor although the softening temperature of the coating material is high.

[INDUSTRIAL APPLICABILITY]

[0115] The embossed release paper according to the invention is useful for producing the synthetic leather.

15 [BRIEF DESCRIPTION OF THE DRAWINGS]

[0116] [Fig. 1] Fig. 1 is a diagram showing an embodiment of a production process of a release paper according to the present invention.

20 [Explanation of Reference numerals]

[0117]

1: leading roll

2: emboss roll

3: backup roll

4: winding roll

25 5: paper with curable coating film

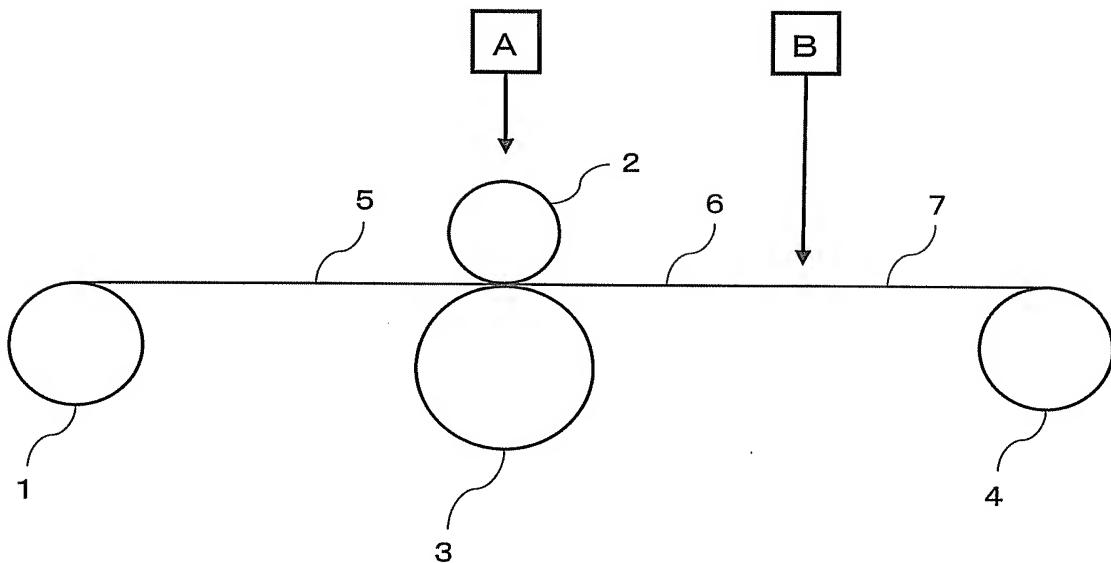
6: paper with an embossed curable coating film

7: embossed release paper

A: step of embossing

B: step of ionizing radiation irradiation

[TITLE OF DOCUMENT] DRAWINGS
[FIGURE 1]



[TITLE OF DOCUMENT] ABSTRACT

[Abstract]

[Object of the Invention] To provide an embossed release paper which has excellent heat resistance and separability from a two-pack 5 curing type adhesive, that is, can be applied in the production of all of synthetic leathers, excellent releasability after repeated use and embossability, and can be obtained at low cost

[Means for Attaining the Object] There is provided an embossed release paper for synthetic leather production, comprising at least 10 paper as a support and an ionizing radiation cured film provided on the paper, the upper part of the cured film having been embossed, characterized in that the ionizing radiation cured film has been formed by applying an ionizing radiation to a coating material comprising at least an ionizing radiation curing composition having a softening point 15 of 40°C or above, to cure the ionizing radiation curing composition, the ionizing radiation curing composition comprising a product of a reaction of an isocyanate compound with an (meth)acrylic compound containing an (meth)acryloyl group and reactive with the isocyanate compound.

[Selected Figure] Figure 1